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OUTCOMES OF THE RILEM ROUND ROBIN ON DEGREE OF REACTION OF SLAG AND FLY ASH IN COMPOSITE CEMENTS

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Abstract
Working group 2 of the RILEM TC 238-SCM organized a round robin test to compare the protocols of different laboratories to determine the degree of reaction of two slags, a calcareous and a siliceous fly ash in binary mixes with Portland cement. The techniques used were: selective dissolution, analysis of the differences in portlandite content from thermogravimetric analysis, X-ray diffraction with PONKCS (partial or no known crystal structure) refinement, and scanning electron microscopy with image analysis. As each laboratory followed their own protocols, the collective assessment of the results provided an idea of the maximum inter-laboratory variability, which should be universally valid. This study assesses the accuracy and precision of the four techniques investigated and with respect to each of the materials studied.

1. Introduction

Working group 2 of the RILEM TC 238-SCM: Hydration and microstructure of concrete with supplementary cementitious materials (SCMs) carried out a comparison of the practices in six European laboratories (named A-F) to determine the degree of reaction of slag and fly ash in composite cements. The quantification of the degree of reaction of SCMs in hydrated cement is challenging and each of the currently available methods has both advantages and disadvantages. The abovementioned committee have recently summarized those techniques in [1], but the actual inter-laboratory performance has never been tested. This paper presents general results of this study and a full paper is in preparation.

2. Materials

The materials used in this study were portland cement PC, slag S1 and slag S2, siliceous fly ash SFA, calcareous fly ash CFA, and quartz Q inert filler. The chemical and phase composition of the raw materials are shown in Table 1. The two slags studied were > 99% amorphous. The particle size distributions of the raw materials were measured by laser diffraction using a Malvern MasterSizer S and are presented in Figure 1.

Table 1: Chemical and phase composition [wt.-%] of the raw materials measured by XRF and by XRD-Rietveld refinement respectively.

	PC	**S1**	**S2**	**SFA**	**CFA**	**Q**		**PC**	**SFA**	**CFA**
Al_2O_3	5.7	11.5	11.6	24.4	19.8	1.0	C_3S	66.2	-	-
SiO_2	19.3	36.4	36.7	70.8	42.3	97.9	C_2S	7.0	-	2.5
CaO	63.7	40.7	38.9	0.1	20.7	0.0	C_3A	6.5	-	1.0
Alkalis	1.4	0.5	0.9	0.7	1.8	0.8	C_4AF	11.9	-	2.0
MgO	1.6	7.4	7.8	0.2	2.2	-	Quartz	0.2	14.9	1.3
Fe_2O_3	3.6	1.4	0.5	2.2	8.2	0.0	Mullite	-	19.3	-
SO_3	3.2	2.1	2.8	-	1.4	-	Free lime	0.2	-	1.7
							Anhydrite	4.6	-	1.8
							Arcanite	2.1	-	-
Others	1.5	-	0.8	1.6	3.6	0.3	Amorphous	-	65.8	89.7

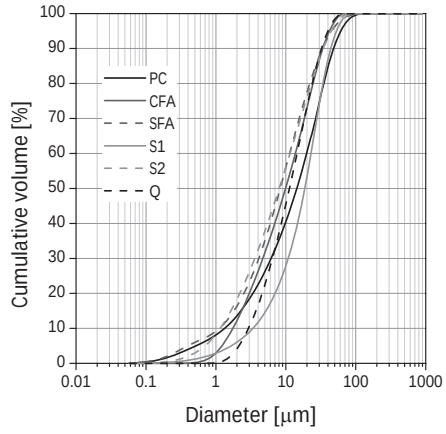

Figure 1: Particle size distributions measured by laser diffraction.

The study was carried out on paste samples: PC + 40 wt.-% slag and 30 wt.-% fly ash. Reference samples contained PC and 40 wt.-% and 30 wt.-% of quartz inert filler. The powders were mixed with water (water/binder ratio 0.4) using a laboratory mixer at 1600 rpm. The pastes were seal-cured for 1, 7, 28 and 90 days at 20 °C. After curing, discs of around 2-3 mm thickness and 33 mm diameter were cut from the paste cylinders. To stop hydration these discs were kept for 7 days in isopropanol and then 7 days in vacuum desiccator. One

laboratory prepared the samples, which were then sealed in vacuum bags and distributed to the participants. Before experiments, the participants removed by gentle grinding the outer layer of the samples, which may have carbonated.

3. Methods

Below basic information is given on the techniques used. Details will be presented in the full publication. Each participating laboratory could choose the techniques to apply and follow their own protocols.

Selective dissolution for fly ash and its cements was carried out using HCl + salicylic acid + methanol, similarly to the European standard CEN/TR 196-4 (2007). The residue of raw fly ashes in salicylic acid + HCl was: for SFA 98-99 wt.-% and for CFA 70-80 wt.-%. Such low residue of CFA made it unacceptable for the determination of the degree of reaction by this method. The calculation of the degree of reaction of SFA was done according to [3].
Selective dissolution of slags and slag cements was carried out using EDTA+TEA+DEA water solution. The residue of slags in EDTA+TEA+DEA was 90-95 wt.%, which is rather low but still acceptable. The degree of reaction of slag in the PC-S pastes was computed according to [2].

Calculation of the degree of reaction of SCMs based on the portlandite difference was carried out on data from thermo-gravimetric measurements on PC-SCM and PC-quartz samples. The latter were used to account for the filler effect of SCMs. One laboratory computed the degrees of reaction of the SCMs following the procedure of Pane and Hansen [4]. The others followed a mass-balance approach, in which Ca required from portlandite and Si coming from the SCM to form C-S-H are balanced. The Ca/Si ratio of the C-S-H needed for this calculation was measured by SEM-EDS point analysis.

SEM – image analysis was carried out on polished sections of epoxy-impregnated paste discs coated with ~15 nm of conductive carbon. Unreacted slag was quantified using BSE images and EDS maps of Mg (lab B) or Mg, Ca, Si (lab E). Unreacted fly ash was segmented using high quality EDS maps of Al, Si and Ca as in [8]. The degree of reaction of the SCMs was computed from the difference between initial and measured amount of SCMs.

X-ray powder diffraction measurements were carried out on raw SCMs and on ground pastes with CuKα radiation (source at 45 kV, 40 mA) and angles 5-70 °2θ. Rietveld refinement was carried out on the background, the unit cell parameters and the Lorentzian peak broadening. Amorphous phase models for PONKCS were prepared based on the scans of raw materials and included in the refinement to quantify the amount of unreacted SCMs.

4. Results

Figure 2 presents the results of the four techniques studied, in which the points correspond to the mean degree of reaction and the whiskers show min-max values. The global mean was

calculated as an average of means. This presentation was chosen, as elaborate statistics on the small data set available would be misleading.

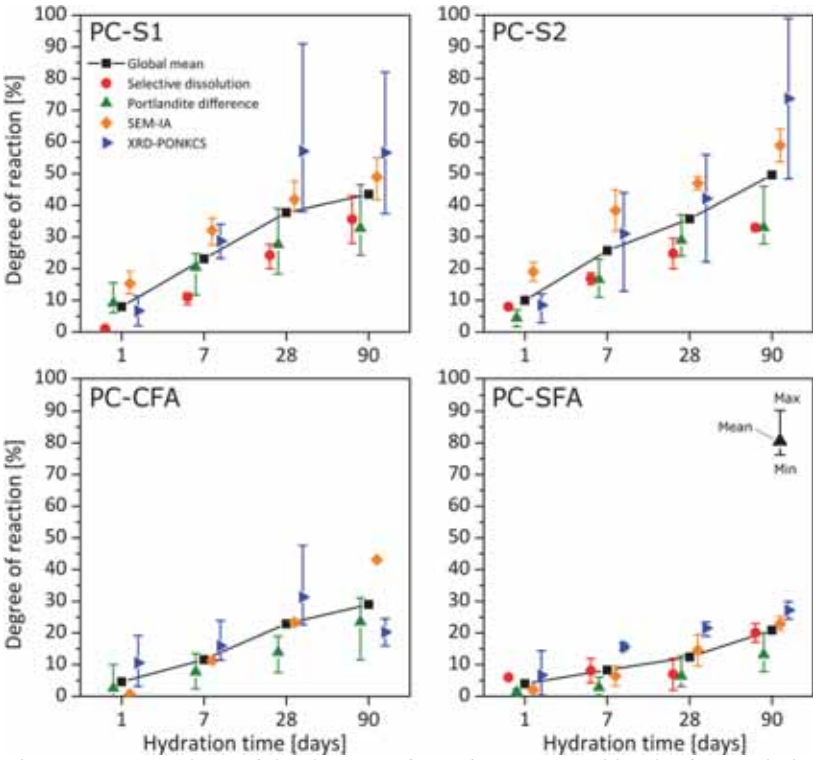

Figure 2: Comparison of the degrees of reaction measured by the four techniques studied.

The main observation from Figure 2 is that the precision of the determination of the degree of reaction of SCMs in hydrating cement pastes is quite low, mostly around ± 10 %, and at best around ±5 %.

Selective dissolution based on EDTA for slag cements underestimated the reaction compared to the global mean. Selective dissolution of siliceous fly ash pastes done with salicylic acid + HCl seemed to work fairly well, but failed completely for the calcareous fly ash pastes.

The degrees of reaction calculated from the portlandite difference were in the low range too. This technique is sensitive to the portlandite content measured since the reaction of slags and calcareous fly ashes consumes little portlandite. Imprecise determination or an estimation of the Ca/Si of the C-S-H may lead to further errors.

SEM-IA was able to measure the reaction of all the SCMs studied, but tended to overestimate the degrees of hydration of slags. This may have been due to unresolved fine particles, which regards the fly ashes too although not observed in the results of this study.

By far the largest variations were observed for the XRD-PONKCS. For PC-SFA the results of the different laboratories were much more comparable, but this is because the degrees of reaction were lower. There is no strict protocol of how model amorphous phases should be prepared and refined. Further, a correct definition of the background is challenging and an overlap between the contribution of the SCM and the C-S-H may hinder correct refinement.

5. Conclusions

The precision of the determination of the degree of reaction of SCMs was assessed by a round robin test of six laboratories. The results indicated that it is generally impossible to determine the degree of reaction of SCMs with precision better than ± 10 %, and at best ± 5 %. As each laboratory followed its own protocols these results are expected to be universally applicable.

As for each of the techniques studied: The degrees of reaction were systematically low for the selective dissolution and this technique failed for calcareous fly ash. Calculations based on portlandite difference may be very sensitive to the portlandite content measured and the Ca/Si ratio of the C-S-H. SEM-image analysis could tackle all the SCMs studied, but may overestimate the degrees of reaction due to unresolved fines. XRD-PONKCS had rather low accuracy and seems very sensitive to the way it is carried out. An improved, strict and careful protocol should be prepared and verified before this method is more widely used.

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